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PROGRESS REPORT

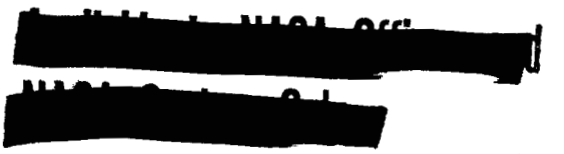
for the period

July 15, 1963 - July 15, 1964

Grant NsG-117-61

To

National Aeronautics and Space Administration
Washington, D. C.



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1. Ni-ThO_2 and Ni-Mo-ThO_2 Alloys Produced by Selective Reduction

It was the purpose of this study to determine if suitable oxide dispersion strengthened structures could be produced with good room temperature properties and high creep-rupture properties at 1800°F, or higher, utilizing mixtures of sub-micron oxides as the starting point.

Because this study will be published by Powder Metallurgy (London) in October 1964, detailed description of the results will not be undertaken here. Preprints will be available within one month, at the latest.

Two of the major problems in producing dispersion strengthened alloys are those of obtaining sub-micron oxides (less than 0.05 micron), and sub-micron interparticle spacing (less than 0.5 micron). If metal powders are utilized, the particle size must be less than 0.5 micron for optimum results. This is both difficult and expensive to do. If internal oxidation is utilized, powders may be coarser, but oxidation resistant systems or complex alloys are ruled out. Similar types of problems are encountered by other alloy preparation techniques.

One of the more attractive alloy methods would utilize ultra-fine oxides of reducible metals blended with or coated by reduction-resistant refractory oxides. Reducible oxides would include those of iron, cobalt, copper, manganese, nickel, molybdenum, and tungsten. ThO_2 was selected as the refractory oxide to be achieved by decomposition of thorium nitrate.

The reducible oxides chosen were NiO and MoO_2 to produce ultimately Ni-ThO_2 and Ni-13% Mo-ThO_2. NiO was available as 0.5 micron material and MoO_2 was milled to 0.6 micron.

Reduction of NiO and MoO_2 was readily accomplished below 1000°C in hydrogen, removing in the meantime water vapor and nitrous oxide gases from the decomposed thorium nitrate.

The fine sub-micron metallic powders alloyed without difficulty during the heating cycle to the extrusion temperature, but in particular during hot extrusion at 1092°C.

The Ni-ThO_2 alloys (3.5 to 9 volume percent thoria) showed some oxide stringering, nevertheless values of 125,000 to 145,000 psi yield stress and 140,000 to 155,000 psi tension stress were recorded at room temperature, with ductility values ranging from 3 to 11 percent elongation. At 982°C all the Ni-ThO_2 alloys except the 3.5 percent ThO_2 alloy showed instability breaks between about 10 and 50 hours. Retained NiO was assumed from structure considerations and checked later (reported below, see section 4).

The Ni-Mo-ThO_2 alloys (3.5 to 9 volume percent thoria) showed unusually uniform oxide dispersions with little difference observable in comparing longitudinal and transverse sections. Yield strength and tension strength values on average were 15,000 to 20,000 psi greater than for the Ni-ThO_2 alloys and ductilities slightly lower.

At 982°C the Ni-Mo-ThO_2 alloys showed no instability breaks out to 100 hours life, yielding for the strongest alloys a stress for rupture in 100 hours of 10,000 to 11,000 psi, interesting strength values comparable to those of TD-nickel and approaching those of the best age-hardened nickel-base super alloys. In longer time tests, based on the flat slopes of these log stress versus log rupture time curves, strength superiority is foreseen. Higher temperature tests are currently under way, the first at 1093°C.

Cold swaging of several of the extruded Ni-ThO_2 and Ni-Mo-ThO_2 alloys resulted in significant 982°C strength improvements. For example, a Ni-Mo-5 v/o ThO_2 alloy showed an increase in stress for a 100-hour rupture life from about 7000 to 9000 psi, an improvement of almost 30 percent.

Based on the cold work studies, and utilizing intermediate low temperature anneals (700 to 900°C), a model is suggested of the strengthening mechanism by cold work.

2. The Structure and Properties of Dispersion Strengthened Alloys In Particular, the System Ni-TiC

Introduction

One of the limitations of oxide strengthened alloys is that they display relatively low strength properties at room temperature when compared with the common age-hardened nickel-base super alloys. On the other hand, oxide dispersion strengthened alloys offer much greater high temperature strength potential than the super alloys above about 982°C.

Age-hardened alloys, the strongest of which are structurally characterized by dispersed intermetallic particles whose size and interparticle spacing are considerably finer and more uniform than that found in the metal-metal oxide alloys, are considerably stronger than metal-metal oxide alloys at low to intermediate temperatures. They are unfortunately subject to re-solution of the precipitate, followed by growth and coalescence, at a temperature as low as 0.5 T_m. In addition, time of exposure at high temperatures plays a much larger role in the structure stability of these alloys compared to the metal-metal oxide alloys.

It is believed that aged alloys derive their high strength, in part, from intense elastic strain fields around closely spaced coherent particles. The volume fraction of such particles in high strength alloys is often large (30 percent in age-hardened Ni-base alloys). Unfortunately, growth of these particles at high temperatures leads to a loss of coherency with attendant loss of strength; strength losses are also associated with the resultant coarser interparticle spacing. In contrast, the metal-metal oxide alloys have a more uniform distribution of internal energy and the total particle content is usually lower than in the age-hardened alloys, accounting in part for the lower strength at lower temperatures.

It would be desirable to achieve an alloy system by dispersion techniques which could incorporate the better structural and property combinations of both types of alloy systems. Accordingly, the plan of this work was to attempt to introduce a stable, hard, refractory dispersoid, such as TiC or TiB_2, which might be fine enough to be coherent with the matrix and yet maintain some degree of stability at high temperatures. In this way, for a given volume percent of dispersoid, the effective interparticle spacing would be smaller and better low temperature strength would be achieved.

Diffusion Studies

In order to determine the compositions of reactants and conditions necessary for producing a dispersion of TiC or TiB_2 in Ni, a series of diffusion studies were performed. Diffusion couples were made by matching Ni-Ti buttons, ranging in composition from 1 to 10 percent Ti, with Ni-C alloys ranging in composition from 0.1 to 0.5 percent C, or Ni-B alloys ranging in composition from 0.1 to 5 percent B. Couples

made from all possible combinations of these alloys were treated for 50 and 100 hours at 700, 800, and 900°C.

In the Ni-Ti:Ni-C alloys, a fine dispersion of TiC formed on the Ni-Ti side of couples containing more than 5 percent Ti and 0.1 percent C. The dispersoid was identified by means of carbon extraction replication and electron diffraction.

In the Ni-Ti:Ni-B diffusion couples, however, TiB_2 was not formed on the Ni-Ti side. Rather, a ternary compound, with the composition $(Ni_{21},Ti_2)B_6$ formed. This phase was massive and formed at the interface of the diffusion couple; as such it did not appear to lend itself to dispersion strengthening potential.

Strain Field Studies

In addition to the diffusion studies, preliminary studies were also performed using transmission electron microscopy. The intent was to observe the strain fields associated with the second phase particles in these dispersion strengthened systems.

The strain fields appear as dark double lobe-shaped contrast effects when observed in transmission electron microscopy. The size of the contrast effect is proportional to the amount of strain around the particle.

Strain fields were studied in the Cu-Al_2O_3, Ni-Al_2O_3, and Ni-TiC systems. The first two systems were prepared by internal oxidation of Cu-0.23 percent Al and Ni-0.45 percent Al alloys, while the Ni-TiC alloy was prepared by aging a supersaturated Ni-6 percent Ti - 0.2 percent C composition. Specimens of these alloys were electrolytically thinned and observed on a Hitachi HU-11 electron microscope operated at 100 KV. The electrolytes used for the thinning of the specimens were 23 percent perchloric acid, 77 percent glacial acetic acid for Ni-Al_2O_3; 33 percent nitric acid, 67 percent methyl alcohol for the Cu-Al_2O_3 alloys;

390 ml H_2SO_4, 290 ml H_2O for the Ni-TiC alloy.

Strain fields were observed around the fine Al_2O_3 particles in copper which had been internally oxidized for 45 minutes at 800°C. These particles were about 60 - 100 Å in diameter and suggested that the structure might be coherent because of the size of the strain fields. Positive proof could not be advanced.

Specimens of Ni-Al were internally oxidized for various times at 700, 800, 900, and 950°C. It was found that the Al_2O_3 particle size obtained in the Ni-Al_2O_3 system was an order of magnitude coarser than that in the Cu-Al_2O_3 alloy. The reason for the smaller Al_2O_3 particle size in copper was that the diffusion rate, and solubility of oxygen in Cu are very much greater than in Ni at the same homologous temperature. Thus a considerably higher degree of oxygen supersaturation is obtained in the Cu-Al system, resulting in a large nucleation rate, and hence a smaller particle size and interparticle spacing.

There were no strain fields associated with the coarse Al_2O_3 particles in Ni.

Fine particles of TiC were precipitated in the Ni-6 percent Ti - 0.2 percent C alloy during aging of 700°C after a solution treatment of 24 hours at 1200°C. These particles did exhibit strain field contrast for particles as coarse as 300 Å, however this could not be proven to be due to coherency, unless coherency existed at the tips and corners of the TiC platelets.

The orientation relationship of the TiC in nickel was found to be:

$$(111)_{matrix} \parallel (11\bar{2})_{TiC}$$

$$[1\bar{1}0]_{matrix} \parallel [111]_{TiC}$$

Bulk Alloy Preparation and Testing

Having determined the conditions required to precipitate TiC in nickel, attempts were made to produce bulk alloys containing a

DISPERSION STRENGTHENED SYSTEMS

This report covers two six-month periods, from July 15, 1963 - July 15, 1964, and covers the following topics:

1. Ni-ThO_2 and Ni-Mo-ThO_2 Alloys Produced by Selective Reduction

2. The Structure and Properties of Dispersion Strengthened Alloys, in Particular, the System Ni-TiC

3. Internal Oxidation of Copper-Nickel-Aluminum Alloys

4. High Temperature Properties and Stability of Ni-ThO_2 and Ni-Mo-ThO_2 Alloys Produced by Selective Reduction of Mixed Oxides

5. ThO_2 Dispersion Strengthened Niobium

6. Intermetallic Compound-Ductile Binder Composite Materials

Items 2 and 6 represent topics which had been initiated under other programs but were completed under NASA sponsorship because they were able to supply valuable information regarding the nature and behavior of dispersion strengthened alloys. Their contribution will be significant.

Publications resulting during this period are the following:

1. "Particle Coarsening in a Copper-Silica Alloy", by N. Komatsu and N. J. Grant", Trans. AIME Met. Soc., 230, August 1964, p. 1090.

2. "ThO_2 Dispersion-Strengthened Ni and Ni-Mo Alloys Produced by Selective Reduction", by J. G. Rasmussen and N. J. Grant: Accepted for publication in Powder Metallurgy, under sponsorship of the Journal of the Iron and Steel Institute and the Institute of Metals, London, England.

In addition, three or four papers are in the course of preparation for publication.

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fine dispersion of TiC and to determine their mechanical properties at room temperature and high temperatures.

The first alloy was prepared by mixing (-275 + 325) mesh powders of Ni - 6 percent Ti and Ni - 0.2 percent C. These powders were compacted and extruded at 815°C at an extrusion ratio of 15 to 1. The structure of this alloy in both the as-extruded and as-annealed conditions was duplex in nature in that there were areas containing a dispersion of TiC and areas devoid of TiC. This was due to the difference in the diffusion rates of Ti and C. The carbon diffused into the Ti-rich regions, forming TiC, before the Ti could diffuse into the carbon-rich regions; thus the Ni-C areas became depleted of carbon, leaving only pure Ni there.

In order to overcome this difficulty, it was decided to add elemental carbon to the Ni - 6 percent Ti alloy. The first attempt involved the use of gas carburization. Methane gas was decomposed on the surface of Ni - 6 percent Ti chips; however, at temperatures below 850°C the decomposition reaction was dependent on the surface condition of the chips. The nickel-titanium served as a catalyst for the reaction; hence, its surface condition was very important for the process. Incomplete or non-uniform decomposition of the methane resulted in non-uniform carburization. Again a duplex structure was obtained in an extruded alloy.

It was then decided to add carbon as carbon black mixed with -325 mesh Ni - 6 percent Ti powder. Two alloys were made in this way; one contained enough carbon to form 5 volume percent TiC, the other contained enough carbon to form 10 volume percent TiC. After extrusion

at 815°C, at a reduction of area ratio of 19 to 1, a dispersion was formed which was much more uniform than in any of the previous alloys. Room temperature tensile tests were performed on all of the alloys. The results are shown in Table I.

TABLE I

Room Temperature Tensile Properties

Alloy	Condition	0.2% Y. S. psi	U.T.S. psi	Elongation,%
NC-1	as extruded	51,700	88,600	16.1
NC-1	annealed 50 hours at 800°C	47,000	86,800	22.0
NC-2	as extruded	145,000	149,000	9.0
NC-3	as extruded	147,000	149,000	7.5
NC-4	as extruded	*		
Ni-6%Ti+	annealed 800°C	26,000	80,000	55.0

\+ Wrought alloy - solid solution

* Two specimens broke in threads with no plastic deformation at 162,000 psi

NC-1 was prepared by the mixing of solid solution powders; NC-2 by decomposition of methane on Ni-6% Ti chips; and NC-3 and NC-4 by mixing of carbon black with Ni-6 percent Ti powders.

Stress rupture tests were performed on alloys NC-3 and NC-4 at 815 and 982°C. The variation of the stress for 100 hour rupture life with temperature for these alloys, Inconel 700, and Ni - 9 volume percent ThO_2 are shown in Figure 1. It is obvious that the alloys prepared in this investigation are significantly weaker at high temperatures than the alloys representative of the other classes of dispersion strengthened materials.

A reason for the low strength at high temperatures for the alloys prepared in this investigation is the fast rate of growth of the TiC particles. Initially, these alloys are stronger than those made by conventional ingot practice, but any contribution TiC might have on the strengthening of these alloys is lost after a short time at high temperatures. In longer time tests, strengthening depends on more conventional solid solution effects and the presence of bonding forces between the TiC and the nickel alloy matrix. At the lower temperatures, the combination of second phase strengthening and cold work lead to highly acceptable strength and ductility values. These alloys might be quite useful to 650 to 750°C, however, tests were not performed below 815°C.

A technical paper is being prepared to cover in much greater detail the results of this study. Copies should be available in one to two months.

3. Internal Oxidation of Copper-Nickel-Aluminum Alloys

In the past, this laboratory has been successful in producing high strength, high temperature oxide dispersion strengthened alloys by internal oxidation of dilute alloys of copper containing either aluminum or silicon and of nickel containing beryllium, aluminum, titanium, chromium, and silicon.

The strongest as yet reported alloys were produced in the Cu-Al_2O_3 system for temperatures from 450 to 850°C. Strength improvements range from 2x to 30x that of the best commercial copper alloys.

Similarly Ni-Al_2O_3 alloys were made yielding stress for a 100-hour life at 982°C of about 10,000 psi. This value is not as good on a homologous temperature scale as that of the Cu-3.5 volume percent Al_2O_3 alloy, but is comparable to values reported for other nickel-metal oxide alloys, and better than most commercial nickel-base alloys above about

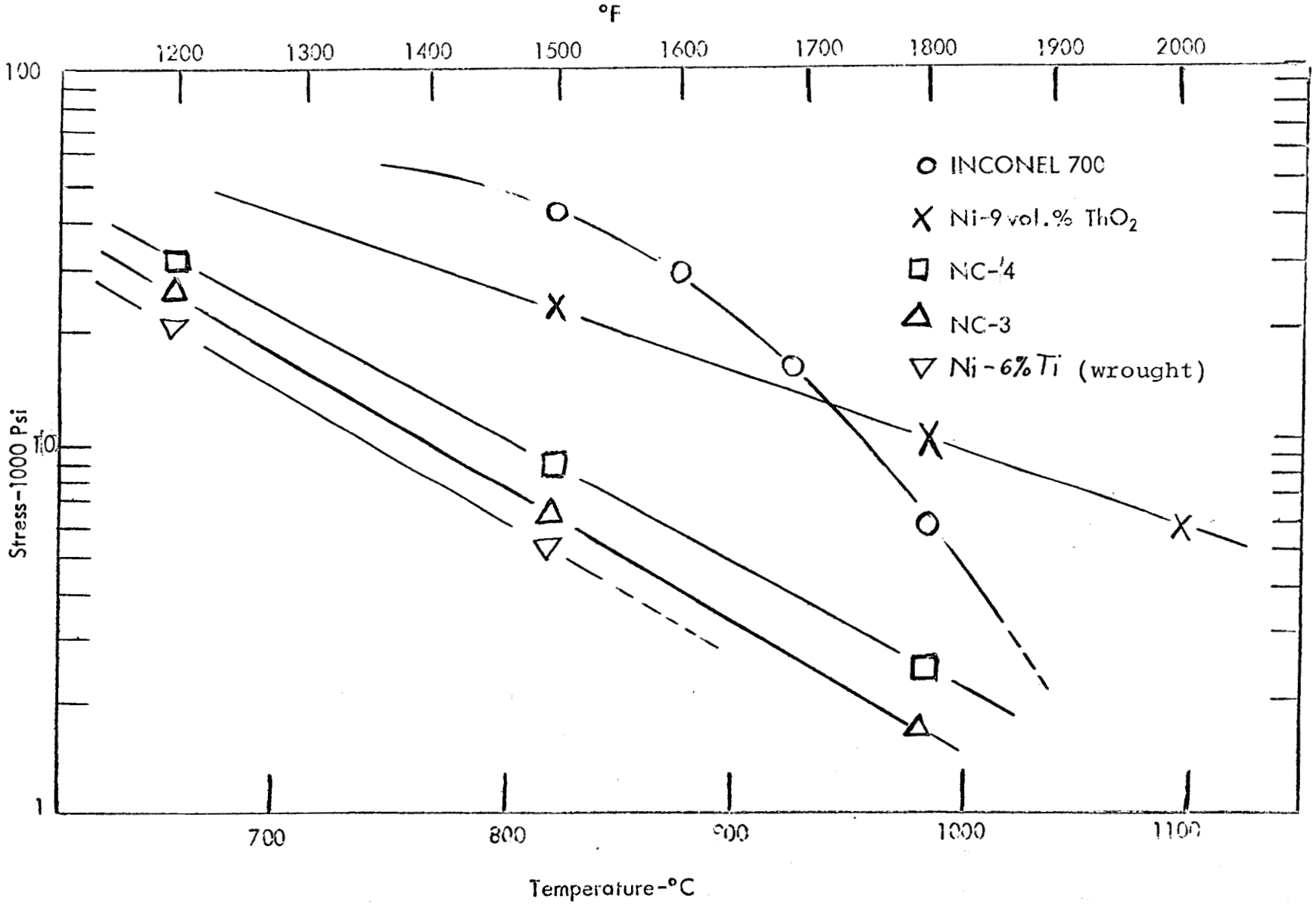

Figure 1 The Variation of Stress for 100 Hour Rupture Life with Temperature for Inconel 700, Ni-9 vol.% ThO_2, Ni-6% Ti and Alloys NC-3 and NC-4

982°C.

One way of improving further the high temperature potential of such alloys would be to increase the basic strength of the matrix by solid solution hardening. Because the Cu-Ni system is of the solid solution type, and because nickel strengthens copper very significantly, both at room and at elevated temperatures, this system was selected for study.

Procedure and Results

The chemical compositions of the three starting alloys are shown in Table II.

TABLE II

Chemical Compositions of Original Alloys
(Weight Percent)

Alloy	Nickel	Soluble Aluminum	Alumina	Copper
A3	10.16	0.76	0.024	balance
A4	20.11	0.79	0.024	balance
A5	30.07	0.80	0.037	balance

Five procedures were considered for preparation of these alloys, four of them were employed. In common for all alloys, the following conditions were observed:

a) Homogenization of an original cast alloy ingot;

b) Machine milling into coarse chips;

c) Hydrogen treatment of the chips to minimize surface oxides;

d) Rod milling of the chips to make them into fine powder;

e) Hydrogen treatment of the powder;

f) Internal oxidation of the powder;

g) Hydrogen treatment to remove excess oxygen;

h) Vacuum compression and hydrostatic compression;

i) Sintering of the compact in hydrogen;

j) Hot extrusion.

The differences in each procedure came mainly from modifications in the rod milling, internal oxidation, and extrusion. Summaries of the procedures for making the alloys are shown in Table III. Procedure I, surface oxidation method, was not employed. Surface oxidation, followed by diffusion of oxygen into the powder, which was successful for Cu-Al alloys, failed in this instance because of the formation of the spinel $NiO.Al_2O_3$ in copious amounts.

Minor parts of the extruded materials were cold swaged to study changes in strength and ductility with cold work. Table IV lists the materials which were studied in the as-extruded and cold swaged conditions. Though X-ray line broadening studies suggested an extremely fine oxide particle size, optical and electron microscopy showed a much coarser particle size. This would indicate clusters of ultra-fine oxide particles to comprise part of the structure.

Annealing tests showed that the room temperature hardness values of the as-extruded alloys (approximately R_B 80 to 95) did not drop on heating for one hour up to at least 1000°C for some alloys, and up to 1100°C for the best alloys. This establishes the stability of these Cu(Ni)-Al_2O_3 alloys to be as good as that of the spectacular Cu-3.5 volume percent Al_2O_3 alloys reported by Preston and Grant several years ago. Table V shows the room temperature tensile properties of these alloys. Table VI shows the creep-rupture properties at 650°C.

TABLE III

Summaries of Procedures for Making Alloys

Process	I	II	III	IV	V
Rod milling of chips	In air, -20 +28 mesh	In air, -400 mesh	In alcohol with stearic acid, A+H_2 atmosphere, 8.5 hrs.	Same as III, but 18 hrs.	Same as IV
H_2 treatment of rod milled powder	600°C, 1 hr.	800°C, 4 hrs. on multi-tray	750°C, 1 hr. in a boat	620°C, 1 hr., in a boat	Same as IV
Internal oxidation	Surface oxidation and heating in vacuum 900°C, 1 hr.	800°C, 50 hrs., multi-tray, with separate NiO in argon	800°C, 5 hrs., rotary kiln (1 rpm) separate NiO in argon	NiO blended with alloy powder, 800°C, 5 hrs., in boat, in argon	NiO blended with metal powder, 700°C, 30 hrs., in boat, in argon
H_2 treatment after internal oxidation	-	800°C, 1 hr., multi-tray	800°C, 1 hr., rotary kiln	800°C, 1 hr., in boat	700°C, 1 hr., in boat
Compaction and sintering	-	Vacuum and hydrostatic (30 Ksi) compaction, sintered in H_2, 800°C, 1 hr.	Vacuum and hydrostatic (6 Ksi) compaction, sintered in H_2, 750°C, 1 hr.	Same as III	Vacuum and hydrostatic (30 Ksi) compaction, sintered in H_2, 765°C, 1 hr.
Extrusion	-	Iron can, evacuated, 760°C, ratio is 1:20, ram speed is 40 in/min.	Same as II, at 870°C	Same as III	Copper can, evacuated, 760°C, ratio is 20:1, ram speed is 40 in/min.

TABLE IV

Cold Swaging Studies

Material Code	Description
E31	From alloy A3 (10 percent Ni) by Procedure II
E51	From alloy A5 (30 percent Ni) by Procedure II
E41	From alloy A4 (20 percent Ni) by Procedure III
E42	From alloy A4 (20 percent Ni) by Procedure IV
E43	From alloy A4 (20 percent Ni) by Procedure V
S31-1	E31 cold swaged 9.0 percent
S31-2	E31 cold swaged 16.5 percent with intermediate annealing at 650°C for 0.5 hour
S51-1	E51 cold swaged 8.7 percent
S51-2	E51 cold swaged 16.8 percent with intermediate annealing at 650°C for 0.5 hour
S41-1	E41 cold swaged 15.2 percent
S42-1	E42 cold swaged 17.5 percent
S42-2	E42 cold swaged 32.5 percent with intermediate annealing at 650°C for 0.5 hour

TABLE V

Room Temperature Tension Properties

Material Code	Yield, Ksi (0.2 % offset)	Ultimate, Ksi	Elongation, %
E31	61.8	68.8	5.8
E51	72.5	81.8	6.8
E41	36.2	55.5	13.0
E42	69.6	82.2	9.0
E43	81.2	87.2	7.1
Preston and Grant's Cu-3.5 vol. % Al_2O_3	65.1	76.0	13.0
Blucher's Cu-10 % Ni-9 v/o Al_2O_3	32.5	52.1	0.17

TABLE VI

Creep Rupture Properties at 650°C

Material	Stress Ksi	Rupture Life, hours	Minimum Creep Rate % per hour	Elongation %
E31	17.00	0.038	----	5.6
	15.00	1.09	1.13	3.3
	13.70	7.10	0.247	3.1
	12.20	70.8	0.0211	3.0
E51	15.00	0.173	8.33	2.4
	13.50	1.45	0.462	1.9
	12.30	12.0	0.0695	2.3
	11.00	90.6	0.0407	2.9
E41	13.50	0.092	----	7.6
	12.00	0.833	0.852	3.2
	9.00	70.7	0.0112	2.4
E42	16.50	0.015	----	2.5
	13.50	0.502	1.20	1.8
	10.00	106.2	0.00787	1.9
E43	15.50	0.503	1.68	1.9
	12.50	26.3	0.0555	2.6
S31-1	15.00	1.33	1.02	3.5
S31-2	15.00	2.06	0.522	3.9
S51-1	13.50	5.23	0.120	2.5
S51-2	13.50	15.8	0.0778	2.7
S41-1	12.00	0.51	2.31	2.6
S42-1	13.50	3.13	0.252	3.1
S42-2	13.50	18.55	0.0285	3.3

Discussion

At 650°C, Preston and Grant's best copper-alumina alloys produced by internal oxidation (Trans. Met. Soc. AIME, 1961, Vol.221, p. 164) is superior to the present copper-nickel-alumina alloys in creep rupture properties. The main cause for this must be the coarser particle size of the aluminum oxide in the present alloys. Another reason may be counter diffusion of solute aluminum toward the surface of coarse powder particles, producing soft unalloyed cores at the center of particles.

First, a mechanism for the coarse oxide particle size will be considered. In precipitation from solid solution heterogeneous nucleation is generally preferred to homogeneous. With a small degree of supersaturation, homogeneous nucleation occurs with greater difficulty. To achieve homogeneous nucleation a rapid establishment of supersaturation is necessary. In age-hardening alloys, this is done by quenching from a one-phase region to the two-phase region. In internal oxidation, on the other hand, the oxygen which provides supersaturation for solute aluminum is made available by diffusion from the surface of the powder particles. For a rapid transport of the oxygen to achieve large supersaturation one must have two things, that is, a high oxygen concentration at the surface of the metal powder particles, and a high diffusion coefficient of oxygen. In the copper-aluminum system the oxygen source could be cupric oxide, while in the present copper-nickel-aluminum system the oxygen source had to be nickel oxide, which produced a much lower oxygen pressure. Also, the rate of internal oxidation penetration in the Cu-Al alloy was much faster than that in the Cu-Ni-Al alloy. Those differences may be sufficient to cause the large change in the nature of nucleation of aluminum oxide.

For the second problem (counter diffusion of aluminum), the actual distribution of the aluminum oxide was measured by step-wise dissolution and extraction. It was found that the center part of the internally oxidized alloy powder particles had little alumina; this was especially true of the coarser powders.

The room temperature properties of some of the present alloys were better than those reported by Preston and Grant; the reason for this is probably that solid solution hardening is much more effective at low temperatures, and full benefits were achieved.

On average, the Cu-Ni-Al_2O_3 alloys were not as strong as the Cu-3.5 volume percent Al_2O_3 alloy studied by Preston and Grant; however, the slope of the log stress versus log rupture life curve was equally flat, indicating maximum stability of structure. Further, the extremely high recrystallization temperature of these alloys also supports the contention of high thermal and time stability.

It is likely that small changes in processing of the alloy powders to avoid the formation of coarse oxides - possibly formation of NiO - will result in alloys stronger than the Cu - 3.5 volume percent Al_2O_3 alloy while retaining the improved room temperature properties and very high recrystallization temperature.

A technical report will be issued on this study within one month offering much greater detail of various aspects of the program.

4. High Temperature Properties and Stability of Ni-ThO_2 and Ni-Mo-ThO_2 Alloys Produced by Selective Reduction of Mixed Oxides

Utilizing some of the same alloys discussed in section 1, above, supplemented by alloys prepared by the same techniques, the following materials were studied:

TABLE VII

Composition of Alloys

Alloy No.	v/o ThO_2	Mo*	Fe*	Ni*
N1	3.16	-	0.025	bal.
N2	4.60	-	0.005	bal.
NM2	4.44	12.0	0.008	bal.
N3	8.33	-	0.014	bal.
NM3	8.30	12.45	0.016	bal.

* in weight percent; Fe is present as an impurity

Material preparation included cold swaging, with and without intermediate annealing treatments, one hour at 750°C for Ni-ThO_2 alloys, and one hour at 900°C for Ni-Mo-ThO_2 alloys.

Tests and evaluation included metallography, light and electron microscopy, X-ray diffraction, hardness measurements (Vickers) at room temperature after various annealing treatments, room temperature tension tests and high temperature stress rupture tests.

Procedure and Results

Hardness - The microhardness values of the 3 nickel-thoria alloys were only slightly changed by cold swaging. The hardness values for the two higher thoria alloys, for the first small increment of cold work, exhibited an initial decrease and then a sharp rise to a level 7-12 VHN below that for the as-extruded material. The values then held constant beyond about 25 percent reduction of area, out to 72 percent reduction of area. The values for the 3.5 volume percent

thoria alloy exhibited an initial decrease and then levelled off without further rise with continued cold work.

The two nickel-molybdenum-thoria alloys both showed an initial decrease of hardness with increasing cold work, though the magnitude of this decrease is less than that of the nickel alloys. There is again a sharp rise in hardness to a level that remains constant with increasing cold work for the material without intermediate annealing. This horizontal plateau in the curve also starts at about 25 percent reduction of area. The alloy with intermediate anneals shows an initial decrease in hardness with the first amounts of cold work and then a gradual linear increase with further cold work.

Strength and Ductility - The results of room temperature tension tests are shown in Figures 2 and 3 for alloys N1 and N3.

Data for the Ni-Mo-ThO_2 alloys are unavailable because of limited bar stock of alloy NM2 and because of the extreme brittleness of the cold worked NM3 material. Eight of twelve samples of NM3 broke during machining; the others broke during testing, exhibiting brittle fractures.

The properties of N1 (3 percent ThO_2) and N3 (8.3 percent ThO_2) vary considerably from each other, but are consistent for the same alloy. Alloy N1, Figure 2, shows a large, sharp increase in strength with relatively small amounts of cold work, with both tensile strength and yield stress rising in parallel fashion. The effects of intermediate annealing are beneficial but not particularly large. This large gain in strength is accompanied by minor losses in ductility (particularly elongation) on which intermediate annealing has little effect. The extraordinary gain in strength with the first

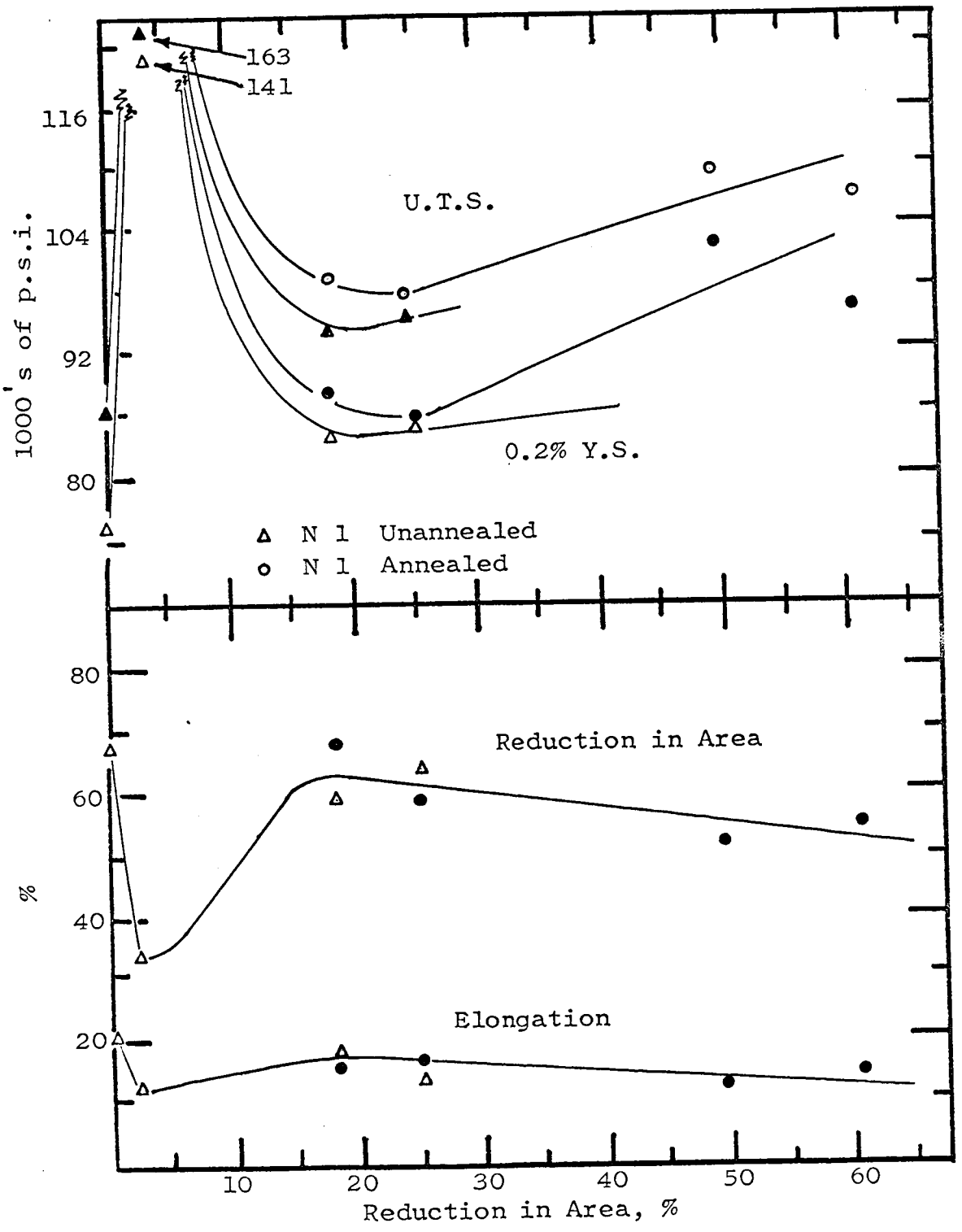

Figure 2. Change in U.T.S., Y. S., and ductility with increasing cold work by swaging, for alloy N1, with and without intermediate annealing treatments.

swaging pass is consistent with a larger, though not proportional, decrease in reduction of area and hardness. Important with respect to the workability of this alloy is that the ductility decreases very slowly with continued swaging, while the strength continues to increase linearly.

Exhibiting different behavior is the high thoria alloy N3, see Figure 3. With increasing cold work, the strength decreases then rises slowly with further cold work. The data for the alloy cold worked with intermediate anneals are limited unfortunately, since most test bars broke during machining or broke in the threaded portion during testing. The data for the one set of annealed samples successfully tested (26.5 percent reduction of area) do indicate significantly greater strength and ductility than for the corresponding unannealed samples.

The initial drop in strength of alloy N3 is matched by an increase in ductility and drop in hardness. Because of the high oxide content and large amount of stored energy due to the extrusion step, there appears to be little chance of increasing the plasticity of this alloy by intermediate annealing steps.

Structure Studies - Photomicrographs taken of the alloys at 1000X show no observable change in microstructure upon swaging or swaging plus annealing, however, this is obviously a limited type of evaluation.

Pinhole back-reflection X-ray photographs show that swaging of alloys N2 and NM2 resulted in significant increases of strain energy, indicated by broadening of the K_{α_I} and the $K_{\alpha_{II}}$ lines to the point where they were poorly resolvable. The samples with intermediate annealing between swaging steps retained patterns very similar to those of the as-extruded material, demonstrating some relief of strain energy.

Back-reflection photographs of alloy N3 showed no significant differences in line width and resolution upon either swaging or swaging plus annealing, indicating saturation with strain energy after the extrusion step.

The high temperature properties of the alloys were determined by means of stress rupture tests in air at 982°C (1800°F) of alloys N2 and NM2. The data from these tests are considered as increases in rupture life (at a constant stress).

In tests as yet incomplete, alloy N2 shows a large increase in rupture life with increasing cold work; this increase was approximately linear on a semi-log plot of rupture life versus area reduction. Intermediate annealing steps of 1 hour at 900°C did not improve, but instead decreased rupture life. Elongation at failure was improved significantly by cold working; this improvement was not affected by intermediate annealing treatments.

Alloy NM2 also showed a very large increase in rupture life with swaging; this increase was even greater with intermediate annealing treatments of 1 hour at 750°C. Elongation at failure also increased with swaging.

Tests of alloys N1 and NM3 were too brittle to test successfully, all exhibiting brittle fractures.

High Temperature Stability - High temperature stability was evaluated by noting room temperature hardness changes as a result of 5 hour anneals at 1000, 1150, and 1250°C for the high thoria alloys (N3 and NM3).

Alloy N3 showed a similar rate of hardness decrease with increasing annealing temperature for all samples, regardless of the amount of cold work or annealing procedures. The 5 hour stability of the alloy is poor, there being a noticeable decrease in hardness

even at 1000°C.

Alloy NM3 demonstrated far greater stability. None of the samples showed a decrease in hardness at 1000°C. The unannealed specimens show a stable structure with no hardness change until slightly after 1000°C, where they show a hardness drop. The swaged plus annealed specimens first show a slight hardness increase with increasing temperature, until at about 1000°C they have a hardness of 5 to 15 VPH points above the as-extruded and the unannealed samples. The amount of this increase seems to increase as the amount of cold work decreases. At 1150°C there is no difference among the samples, but at 1250°C the swaged plus annealed samples have a hardness lower than the unannealed samples, but still above that for the as-extruded material.

Alloys N1, N3, and NM3 were all compared in the as-extruded condition for 1 and 5 hour anneals at the above temperatures. The superior stability of the nickel-molybdenum alloys is clearly evident; there is no hardness difference for the as-extruded material between the 1 and 5 hour anneals until 1250°C, when a large drop in hardness occurs for the 5 hour specimen and only a small drop for the 1 hour test. The two Ni-ThO_2 alloys show differences between the two annealing times at all temperatures, this difference being greater for the alloy having the lowest percentage of thoria.

Discussion

The literature, as well as data from this laboratory, show that cold work after initial hot working is usually beneficial both on high temperature strength and ductility. Literature data, almost without exception, are limited to low oxide content alloys (less than about 3 volume percent), and to alloys which were extruded with a small reduction ratio. As such they are essentially un-cold worked.

These alloys had from 3 to about 9 percent ThO_2 and all alloys were extruded with a high extrusion ratio. As a result the stored strain energy was high, so high that the 9 percent ThO_2 alloys gained little through additional cold swaging. The lower oxide alloys did gain and showed the same pattern of improved hot strength and ductility.

The hardness difference after annealing for 1 and 5 hours at 1000 to 1250°C clearly showed some structural instability in the Ni-ThO_2 alloys. This was substantiated by an instability break in the log stress versus log rupture time plot at 982°C for these same Ni-ThO_2 alloys.

Along the same lines, the Ni-Mo-ThO_2 alloys showed no hardness instability before almost 1250°C. In stress rupture tests at 982°C these alloys showed no instability break in tests up to 100 hours or more.

Since Ni-ThO_2 alloys prepared by techniques other than selective oxide reduction did not show the observed 1000°C instability in hardness or creep rupture, it is evident that an unstabilizing contaminant is present. If one is, it is likely that it might be NiO. This is subject to confirmation.

In current work one additional alloy is being prepared, namely, Ni - 2 volume percent ThO_2 to check on the instability and to confirm the observations regarding the potential for strengthening through cold work (without loss of ductility) in low oxide content alloys

Several months of additional work should permit the writing of a technical report covering this work. It is anticipated that further studies along these lines are highly essential for a better understanding of the variables involved in the fabrication and treatment of oxide dispersion strengthened alloys.

5. ThO_2 Dispersion Strengthened Niobium

This investigation was initiated to determine the practicability of dispersion strengthening a matrix of niobium with oxides whose free energies of formation did not differ greatly from the free energy of formation of the base metal oxide; in order to maintain a stable fine particle size and high temperature strength, the difference should be large. It was expected that there would be an interaction between Nb and the oxide dispersoid at high temperatures, which would give rise to problems of structure and property instability. If any such interaction did occur, and attempt was to be made to determine the extent of such reaction and its effect on mechanical properties. The dispersoids were to be 0.01 micron alundum C alumina, and ThO_2 finer than about 0.05 micron.

Procedure and Results

The base metal was received as niobium hydride, 7 microns Fisher sub sieve size; the H content was 0.88 percent. Originally, the hydride was to have been reduced in vacuum to niobium, then mechanically mixed with Al_2O_3 or ThO_2. Several experiments indicated that there would be problems in handling the pure niobium powder if this were done, as niobium reacts readily with oxygen even at low temperatures.

An attempt was then made to mechanically mix the niobium hydride with the oxide dispersion, vacuum compact (hydrostatic) and then reduce the hydride in compact form; however, experiments on small quantities of material indicated that a violent explosion would occur on heating if this were done on a larger scale. Thus, the matrix and dispersion were first mechanically mixed, then reduced, then compacted.

A) Alumina dispersion strengthened niobium by mechanical mixing - Niobium hydride of 7 microns average size and 0.01 micron alumina were mechanically mixed in a Waring blender to which was added crushed solid carbon dioixde sufficient to maintain a low powder temperature and to minimize briquetting and water pick-up. After mixing, the powders were removed to a vacuum desiccator to remove the remaining carbon dioxide and water.

The mixed powders were placed in a series of nickel boats, arranged in a vertical "train" and heated in a purified argon atmosphere to 815°C (1500°F), the temperature which prior experiments indicated would produce a maximum reduction of the hydride and minimum oxidation of Nb.

The powders were then vacuum compacted in the conventional fashion and hydrostatically compressed at 30,000 psi. The compact was extruded at 1205°C (2200°F) in a mild steel can; the resulting reduction in area was 25:1.

Hardness was measured at room temperature as a function of annealing temperature for 1 hour in vacuum from 200°C to 2000°C in vacua. Metallographic examination, X-ray diffraction and Laue back-reflection photographs followed.

The as-extruded hardness was R_c 37. This value remained constant up to 1200°C when it declined, slowly at first, then markedly at 1800°C. At 1200°C, a pronounced oxide scale is present (its source is to be ascertained) and as the temperature increased, the scale grew in volume and increased in hardness. Attempts to identify the oxide by X-ray diffraction indicate that it is Nb_2O_5.

Photomicrographs show a very agglomerated dispersed oxide phase, even in the as-extruded material. It may be that the temperature at which Nb was extruded is too great to maintain a stable fine dispersion

of Al_2O_3. This was the case with a mixture of Ti and Al_2O_3 extruded at 1000°C, whereby 90 percent of the Al_2O_3 was reduced. Finding a suitable etchant has proved to be difficult. Thus far, the most satisfactory one is a mixture of lactic acid, HNO_3 and HF, although grain boundaries are still not clear.

Room temperature tension tests have been run on as-extruded specimens. They indicate an ultimate tensile strength of 156,000 psi and a ductility of 2.5 percent.

From the limited tests run, it would appear that the Nb-Al_2O_3 system is of much interest and creep rupture tests will be made at 982°C and higher.

B) Thoria dispersion strengthened niobium

a) By prior decomposition of $Th(NO_3)_4.4\ H_2O$ to $ThO_2.X(H_2O)$ and subsequent mechanical mixing with NbH.

Thorium nitrate was decomposed to $ThO_2.x\ (H_2O)$ as described in the work of Mr. Rasmussen (item 1, this report) and then dry ball-milled for 24 hours with NbH. Decomposition was then carried out in the same manner as described for Nb-Al_2O_3 and compaction was begun. After a few seconds of exposure to this atmosphere, the material ignited, melting the nickel boats which held them. This effect did not occur in the small test batch run earlier.

The explanation for this pyrophoricity seems to be two-fold; first, the small size of the Nb particles produced by ball-milling render it more pyrophoric; secondly, nitrate decomposition followed by mechanical mixing yield Nb particles dispersed at random with $ThO_2.x\ (H_2O)$ particles. There is no protection of the fine Nb particle by an envelope of ThO_2 as described for the alloy in the following section.

Accordingly, the procedure was repeated, compacting in a dry box with an argon atmosphere. The alloy was kept sealed in argon when being handled or transferred. After hydrostatic compression at 30,000 psi, it was filed to a diameter of 1.17 inch in the dry box and then extruded at 1065°C, the lowest possible extrusion temperature for Nb in a mild steel can with an extrusion ratio of 12 to 1.

The resulting extrusion appeared to contain several cavities; radiography was performed to see where the core was located. Several sections were taken of the alloy which thus far appears to be brittle. The reasons for this are not yet known. Chemical analyses have not been completed.

b) By ball-milling of NbH and $Th(NO_3)_4.4\ H_2O$ in ethyl alcohol -

Preparation was as follows: combination of required amounts of NbH, $Th(NO_3)_4.4\ H_2O$ and ethyl alcohol in a ball-mill took place, followed by milling for 24 hours. Removal of alcohol and part of the formed by-product took place by vacuum treatment at about 200°C. It was desired to decompose the thoria salt to ThO_2 at about 600°C for minimum ThO_2 particle size, but care had to be taken in order that H coming off from NbH did not combine with NO_2 from the thoria salt and result in an explosion. Preliminary tests have indicated satisfactory results if the NbH and thoria salt mixture are heated slowly in argon. These powders are now ready for decomposition, compaction and extrusion and will be processed shortly.

Some tests on these powders indicate that they are not as pyrophoric as the mechanically mixed powders mentioned above. Upon decomposition of these powders and exposure to air, no glow is observed. It ignites only when lit by a match. This indicates that the ThO_2 particles surround the Nb particles as an envelope and protect

them from the atmosphere. The result is hygroscopic but not pyrophoric.

Planned Work

Aside from the completion of alloy 3, and the running of conventional tests on the mechanical properties of alloys 2 and 3, much work needs to be done on determining the nature of the oxide scale, the extent of its penetration into the material, and whether or not it is due partly to the interaction between the matrix and dispersion.

Chemical analyses will follow further inspection of all as-extruded and temperature - tested specimens by optical and electron microscopy in an effort to determine the nature of interaction between ThO_2 and Nb.

6. Intermetallic Compound-Ductile Binder Composite Materials

Introduction

This investigation was instituted to determine the feasibility of producing high volume content intermetallic compound-ductile binder composite materials by powder metallurgical methods. Many intermetallic compounds exhibit superlative oxidation resistance and good physical properties at elevated temperatures, but are extremely brittle at low temperatures. It is hoped that the composite materials will possess some of the low temperature ductility of the binder metal while retaining the favorable high temperature properties of the intermetallic compounds.

In earlier work four single-phase alloys were produced with compositions lying in the NiAl phase field. It was determined that a composition of about 74 weight percent nickel gave the best high temperature properties; this composition was used for subsequent work in the NiAl system.

In addition, an alloy containing equal amounts of NiAl and Ni_3Al was produced by reaction of 25 volume percent nickel binder with NiAl

during hot extrusion.

New Alloy Preparation

In an effort to prevent a reaction between NiAl and the nickel binder during extrusion, a powder mixture of 90 volume percent NiAl (-325 mesh) and 10 volume percent Inco B nickel powder (approximately 5 microns diameter) was extruded at 815°C (1500°F) (see Table VIII).

An alloy of 90 volume percent NiAl powder (-325 mesh) and 10 volume percent niobium powder (-325 mesh) was extruded at 955°C (1750°F), and one of 75 volume percent NiAl (-325 mesh) and 25 volume percent type 316 stainless steel (-325 mesh) was extruded at 873°C (1600°F) (see Table VIII).

TABLE VIII

Nickel-Aluminum System Powder Compositions

Alloy	Composition (by volume)					
	% NiAl	%Ni_3Al	%Ni	%Nisol.sol.	%Nb	%316 SS
NiAl-74-B3	90	-	10	-	-	-
NiAl-74-C	90	-	-	-	10	-
NiAl-74-D	75	-	-	-	-	25
Ni_3Al	-	100	-	-	-	-
Ni_3Al-NiSS-15	-	85	-	15	-	-
Ni_3Al-NiSS-30	-	70	-	30	-	-

In order to determine conditions wherein alloys in the nickel-aluminum system would be free from reaction between intermetallic and binder, composites of Ni_3Al and nickel-aluminum solid solution were chosen. Ni_3Al, containing 12.4 weight percent aluminum, was argon arc melted using reagent nickel shot and a 50 weight percent nickel - 50 weight percent aluminum master alloy obtained from the International Nickel Company.

This Ni_3Al alloy was homogenized, machined into chips, and dry ball-milled to -325 mesh in a stainless steel mill. A nickel-aluminum solid solution powder containing 7.1 weight percent aluminum was similarly prepared from the same starting materials. Three alloys were made from these powders, containing 0, 15, and 30 volume percent nickel-aluminum solid solution binder, respectively (see Table VIII).

The two powder mixtures containing both Ni_3Al and nickel aluminum solid solution were each dry ball-milled in a stainless steel mill for 72 hours to mix the ductile binder and intermetallic compound thoroughly and to coat the intermetallic compound with a layer of ductile binder. This was done with the intention of producing an extruded structure in which all the hard intermetallic particles would be completely surrounded by a zone of ductile binder. These alloys were loose powder extruded at 873°C (1600°F).

Since an alloy of NiAl with a nickel binder did not appear feasible (due to the presence of Ni_3Al), another system with a similar, cubic, high melting intermetallic compound, but without an intermediate phase between it and the terminal solid solution, was needed. The system cobalt-aluminum was chosen. CoAl, like NiAl, is ordered body-centered-cubic and has a melting point in excess of 1600°C (2900°F). A single composition of CoAl was chosen and a large ingot (12 pounds) of this material was obtained from the International Nickel Company. The composition of this alloy was 28.6 weight percent aluminum. As the binder, two materials were used: pure cobalt powder, and cobalt-aluminum solid solution powder. The pure cobalt powder, obtained from Sherritt-Gordon Mines, Ltd., Canada, was -400 mesh and had a Fisher average size of 3 microns. The cobalt-aluminum solid

solution (5.3 weight percent aluminum), was prepared by argon gas arc melting premelted electrolytic cobalt and reagent quality aluminum pellets. The ingot was homogenized and machined into chips which were subsequently dry ball-milled to -325 mesh in a stainless steel mill.

Two alloys were made with pure cobalt binder, containing 30 and 40 volume percent. Three alloys were mixed with cobalt-aluminum solid solution binder, containing 10, 20, and 30 volume percent, respectively (see Table IX).

TABLE IX

Cobalt-Aluminum System Powder Compositions

	Composition (by volume)		
Alloy	% CoAl	% Co	% Co sol.sol.
CoAl-Co-30	70	30	
CoAl-Co-40	60	40	
CoAl-CoSS-10	90		10
CoAl-CoSS-20	80		20
CoAl-Co-30	70		30

Each of these mixtures was dry ball-milled for 72 hours in a stainless steel mill.

During all ball-mill mixing runs, samples were taken every 24 hours and examined metallographically to determine the degree of mixing with the binder and the comminution of the intermetallic particles. These alloys were extruded at 873°C (1600°F).

Results

Metallographic examination of sections of the extrusion of NiAl-74-B3 (NiAl plus 10 volume percent nickel binder) indicated extensive reaction between intermetallic and binder such that each nickel area was surrounded by a skin of Ni_3Al. This alloy was brittle and the extrusion had both longitudinal and transverse cracks.

The extrusions of NiAl-74-C and NiAl-74-D containing niobium and type 316 stainless steel binders, respectively, were sound and showed no evidence of a reaction between the NiAl and binder.

All of the Ni_3Al series extrusions were good as were the two CoAl extrusions with pure cobalt binder. The series of three CoAl extrusions, however, with 10, 20, and 30 volume percent cobalt-aluminum solid solution binder showed extensive cracks and large variations in alloy core diameter along the extrusion. The tendency was more pronounced with decreasing binder content.

Annealing tests of alloy NiAl-74-C (niobium binder) showed the formation of several intermetallic compounds as concentric layers between niobium and the NiAl areas.

The results of stress rupture tests performed in air at 982°C (1800°F) on alloys NiAl-74-B2 (50 percent NiAl and 50 percent Ni_3Al) and NiAl-74-C are listed in Tables X and XI, and are plotted in Figure 4. Results of similar stress rupture tests performed on pure NiAl are also plotted for comparison. Note that the properties of alloy NiAl-74-B2 are inferior to those of pure NiAl, whereas those of NiAl-74-C are superior. This is in spite of the formation of brittle intermetallic compounds and considerable microcracking in the latter.

Observations

The formation of Ni_3Al in alloys of NiAl with nickel binder cannot be prevented by depressing the extrusion temperature. The formation of additional intermetallic compounds between binder and base compound is not necessarily deleterious to high temperature properties but appears to detract from low temperature ductility. A mixture of Ni_3Al and NiAl has inferior high temperature properties to pure NiAl. The presence of niobium as a binder yields improved high temperature strength properties in NiAl.

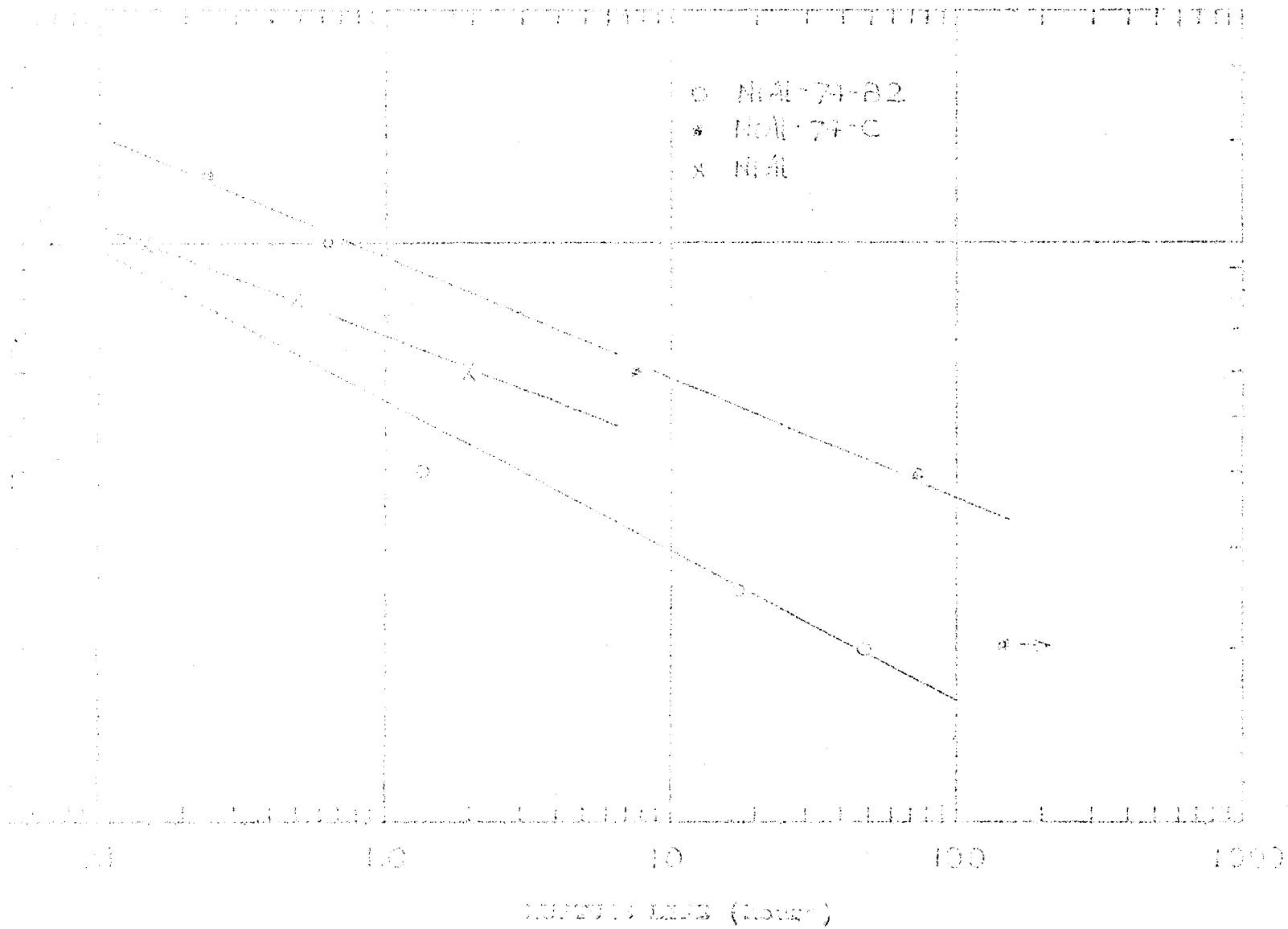

Figure 4. Isothermal creep results of NiAl-74-82, NiAl-74-C, and NiAl at 1300°C

TABLE X

Results of Stress Rupture Results on NiAl-74-B2

Test Temp. °C	Stress psi	Lifetime hours	Reduction of area, %	Elongation %
982	10,000	0.092	37.7	43.0
982	4,000	1.37	33.0	33.5
982	2,500	17.2	62.7	92.0
982	2,000	47.5	66.5	80.0

TABLE XI

Results of Stress Rupture Tests on NiAl-74-C

Test Temp. °C	Stress psi	Lifetime hours	Reduction of area, %	Elongation %
982	13,000	0.24	70.3	71.5
982	10,000	0.629	72.7	74.8
982	6,000	7.57	68.5	93.1
982	4,000	73.4	60.7	73.9
982	2,000	144.3*	13.3*	14.0*

* Test discontinued

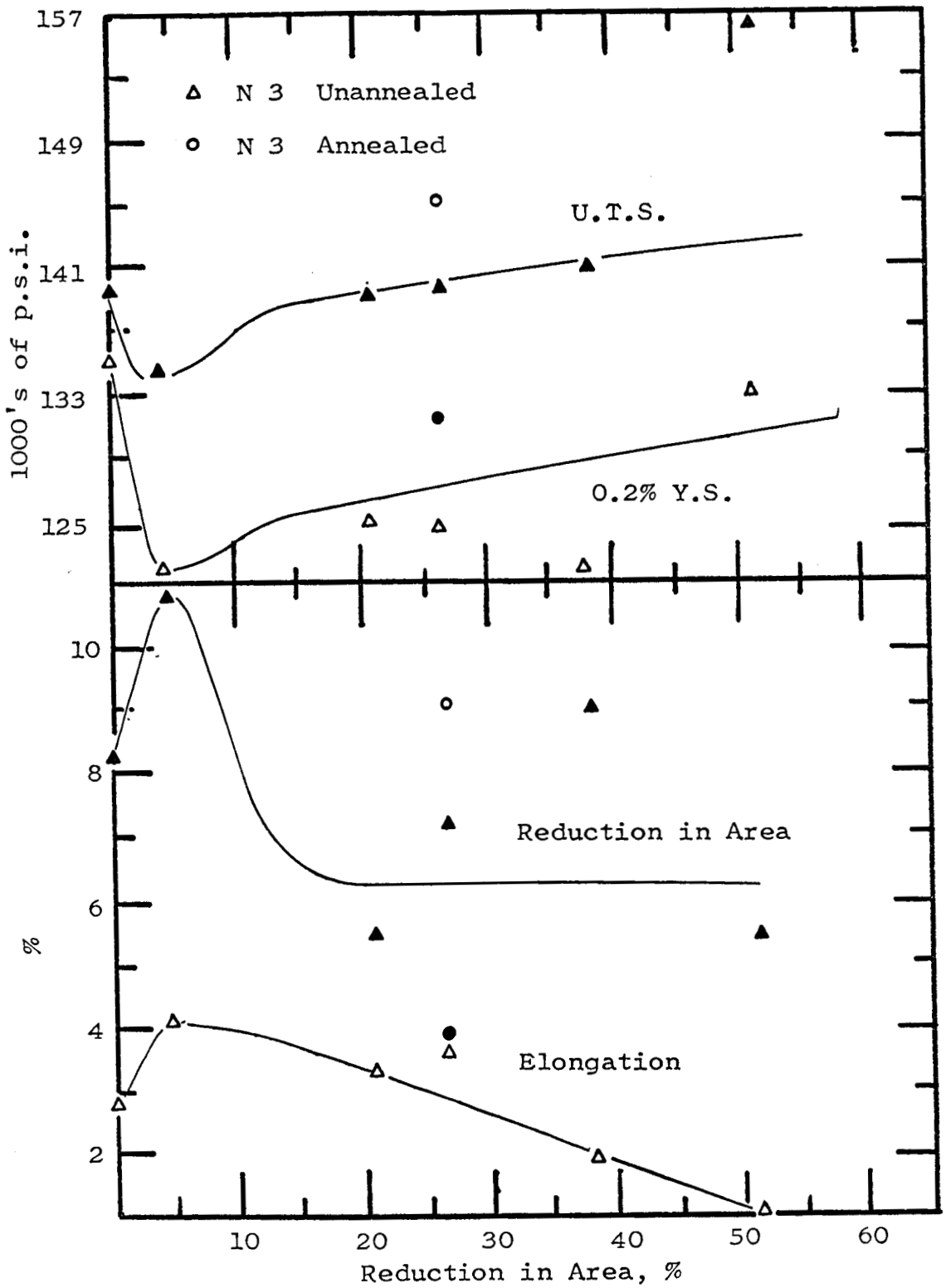

Figure 3. Change In U.T.S., Y. S., and ductility with increasing cold work by swaging, for alloy N3, with and without intermediate annealing treatments.

Future Work

Electron microscope replica studies of CoAl and Ni_3Al alloys are in progress to determine the effectiveness of the binder mixing method employed in achieving a continuous ductile binder film around all hard intermetallic particles.

Stress rupture tests of the remaining sound extrusions are planned to determine the effects of binder composition and content on high temperature properties.

Room temperature transverse rupture tests are planned on all alloys to determine the effects of binder composition and content on low temperature ductility, fracture toughness and elastic properties. Annealed specimens will also be tested to determine the effects of exposure to high temperatures on low temperature properties.

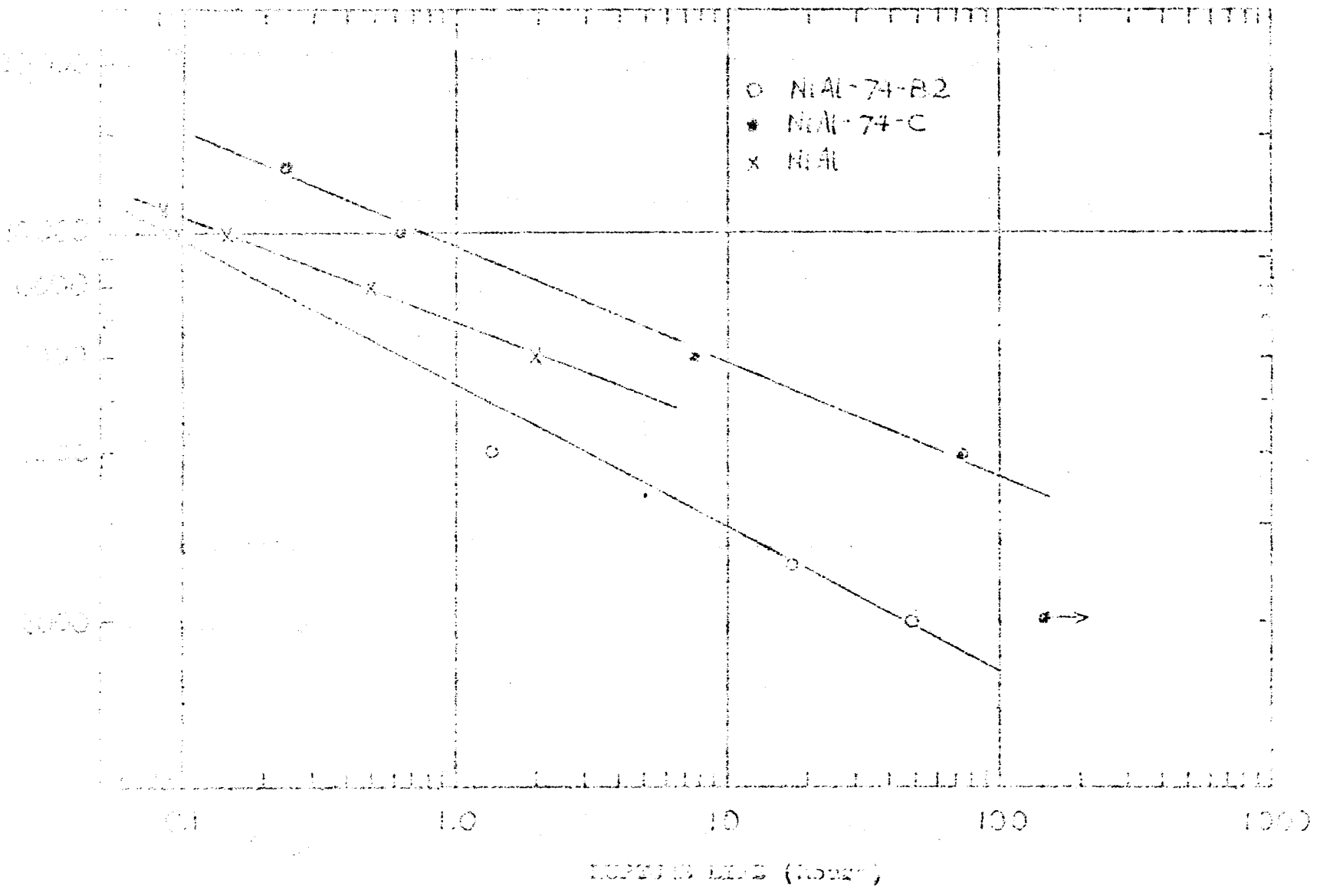

Figure 4. Figure caption [illegible] NiAl-74-B2, NiAl-74-C, and NiAl at 1300°C.

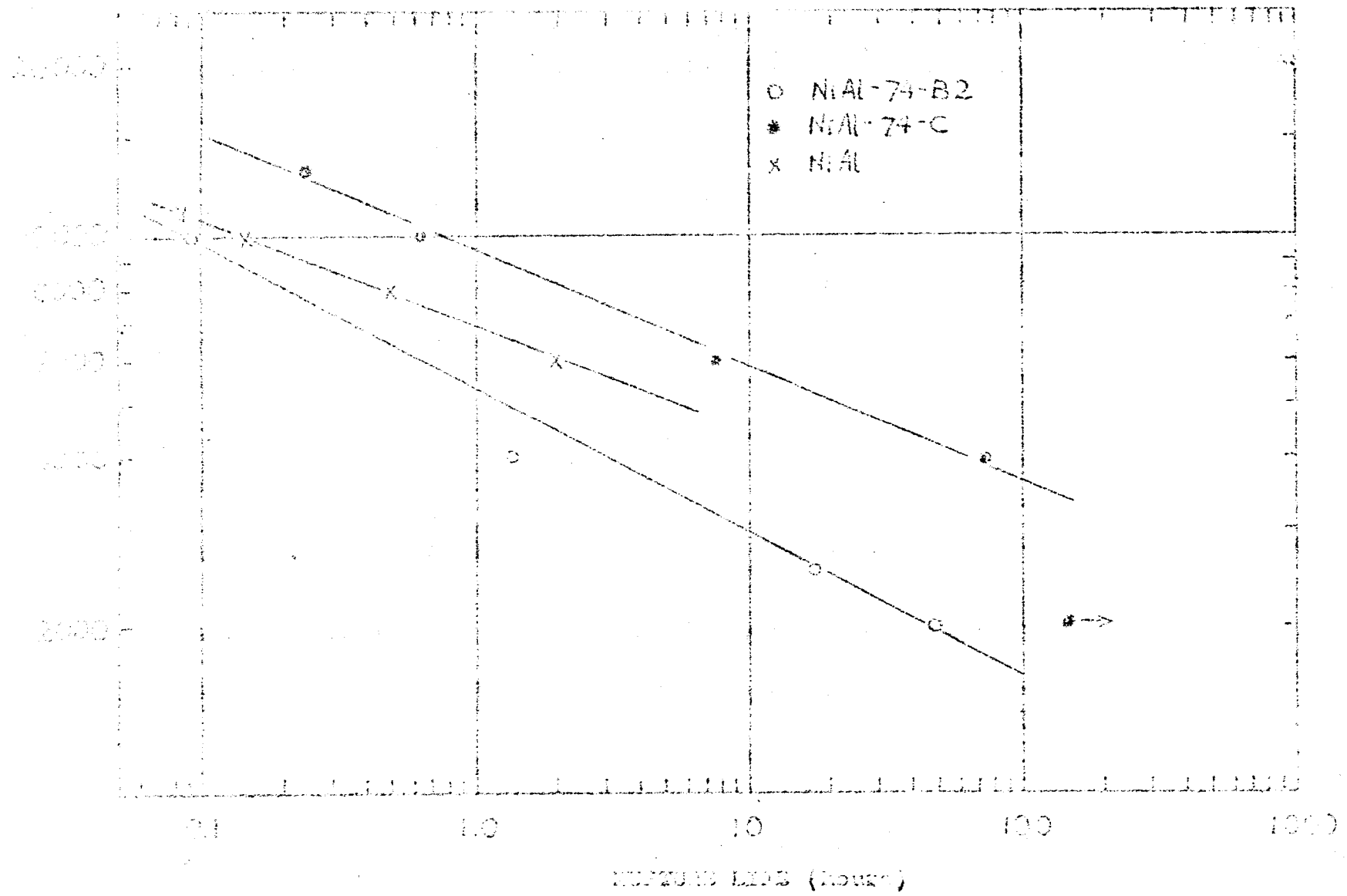

Figure 4. Figure caption text.

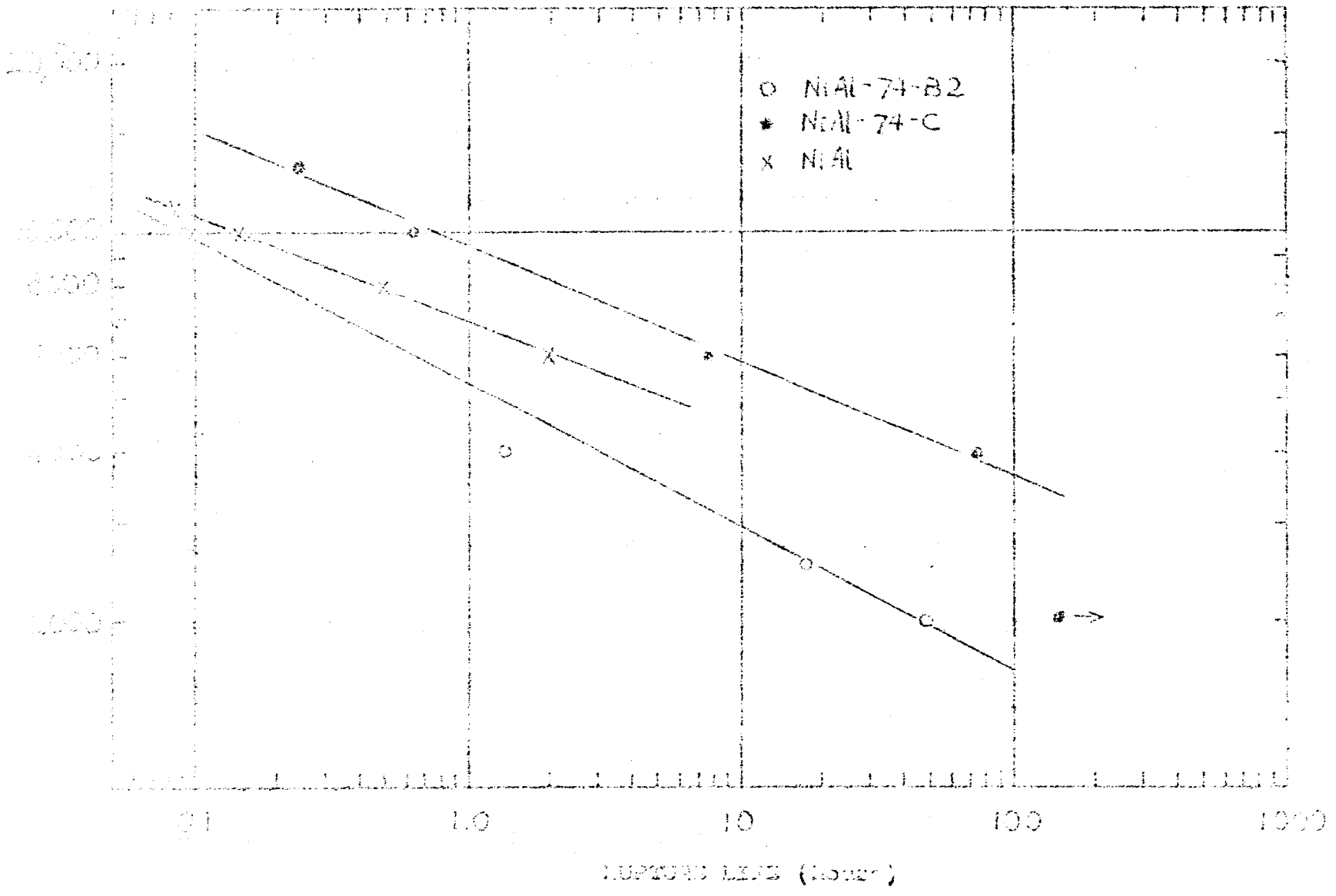

Figure 4. Typical rupture results of NiAl-74-B2, NiAl-74-C, and NiAl at 1800°F.